

# PATENT ABSTRACTS OF JAPAN

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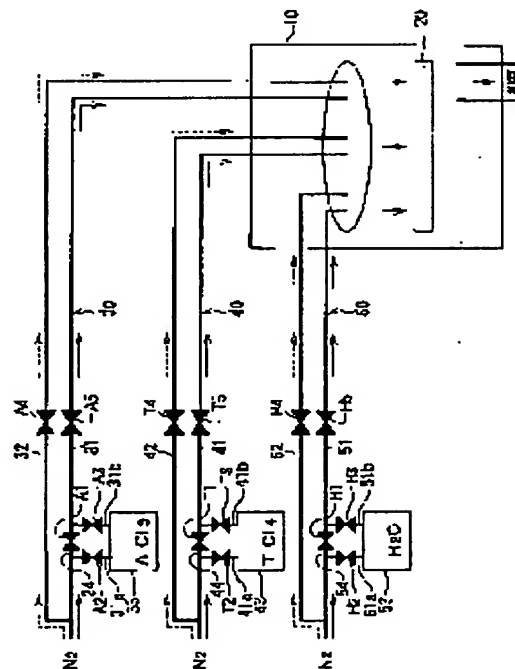
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## (54) THIN FILM FORMING METHOD

(57)Abstract:

**PROBLEM TO BE SOLVED:** To reduce particles in a reaction furnace and in a passage for feeding gaseous starting materials in a thin film deposition method by which gaseous starting materials in which aluminum chloride, titanium chloride and water are vaporized are alternately fed to a reaction furnace 10 to form an alternately laminated thin film of aluminum oxide and titanium oxide on a substrate.

**SOLUTION:** A plurality of gaseous starting material feeding systems 30, 40 and 50 to feed gases into a reaction furnace 10 are provided in accordance with each gaseous starting material. In each gaseous starting material feeding system, by switching valves A4, T4 and H4 and valves A5, T5 and H5, gaseous nitrogen as inert gas can be fed as pulses to the inside of a passage 31 for feeding gaseous starting materials and the reaction chamber so as to generate the variation of pressure. Before a thin film deposition stage, this pulsating feed of gaseous nitrogen is successively performed so that timing is deviated per each gaseous starting material feeding system.



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**CLAIMS**

[Claim(s)]

[Claim 1] By letting the path for material gas supply pass, and supplying the material gas which evaporated the liquid or the solid material into the reaction chamber in which the substrate was installed By supplying inert gas to the interior of said path for material gas supply, and said reaction chamber in the shape of a pulse in front of the formation process of said thin film, in the approach of forming a thin film on said substrate, so that pressure fluctuation may be generated The formation approach of the thin film characterized by performing the clarification process which defecates the inside of said path for material gas supply, and said reaction chamber.

[Claim 2] The formation approach of the thin film according to claim 1 characterized by preparing more than one, and for the material gas supply system for supplying said material gas into said reaction chamber shifting timing mutually, and performing supply of said inert gas by said each supply systems of material gas at said clarification process.

[Claim 3] The formation approach of the thin film according to claim 2 characterized by shifting timing mutually and performing supply of said inert gas by the material gas supply systems of a reactant high combination among said two or more material gas supply systems at said clarification process.

[Claim 4] Said material gas supply system is the formation approach of the thin film according to claim 1 characterized by being about supply of said inert gas with said reducibility gas supply system and said oxidizing gas supply system, and carrying out by having the reducibility gas supply system which supplies the material gas which has reducibility, and the oxidizing gas supply system which supplies the material gas which has an oxidizing quality, and dividing timing mutually at said clarification process.

[Claim 5] Said reducibility gas supply system and said oxidizing gas supply system are the formation approach of the thin film according to claim 4 characterized by being said two or more reducibility gas supply systems and said two or more oxidizing gas supply systems, and carrying out by preparing more than one and summarizing supply of said inert gas at said clarification process, respectively.

[Claim 6] The formation approach of the thin film according to claim 5 characterized by shifting timing mutually and performing supply of said inert gas by each supply system at said clarification process in said two or more reducibility gas supply systems and said two or more oxidizing gas supply systems.

[Claim 7] After installing said substrate by which clarification was carried out after said clarification process and into said reaction chamber and supplying said inert gas like said clarification process, Claim 1 which performs the process which measures the number of particle which adhered on said substrate, and is characterized by performing the formation process of said thin film when there is few measured particle than the number of criteria thru/or the formation approach of the thin film any one publication of six.

[Claim 8] Said number of criteria is the formation approach of the thin film according to claim 7 characterized by the number of particle 1 micrometers [ per two ] or more being one or less the unit area of 1cm of said substrate.

[Claim 9] Claim 1 characterized by performing said clarification process above the service temperature of said path for material gas supply in the formation process of said thin film thru/or the

formation approach of the thin film any one publication of eight.

[Claim 10] Claim 1 characterized by carrying out pressure fluctuation generated by supply of said inert gas at said clarification process to more than the working pressure variation in the formation process of said thin film thru/or the formation approach of the thin film any one publication of nine.

[Claim 11] Claim 1 characterized by the pulse being 10 or less minutes 0.1 seconds or more in supply of said inert gas thru/or the formation approach of the thin film any one publication of ten.

[Claim 12] The formation approach of the thin film which was contained in the raw material container and which is characterized by powdered or supplying inert gas in the shape of a pulse into said raw material container in front of the formation process of said thin film in the approach of forming a thin film on said substrate by supplying the material gas which evaporated the particulate-solid raw material into the reaction chamber in which the substrate was installed so that pressure fluctuation may be generated.

[Claim 13] The formation approach of the thin film according to claim 12 characterized by carrying out pressure fluctuation generated by supply of said inert gas to more than the working pressure variation in the formation process of said thin film.

[Claim 14] The formation approach of the thin film according to claim 12 or 13 characterized by the pulse being 10 or less minutes 0.1 seconds or more in supply of said inert gas.

[Claim 15] Said claim 12 characterized by adjusting to less than \*\*20 kPas of the pressure which is after the process which supplies inert gas in the shape of a pulse into said raw material container, and uses the pressure in said raw material container with the formation process of said thin film before the formation process of said thin film thru/or the thin film formation approach of any one publication of 14.

[Claim 16] The thin film formation approach according to claim 15 characterized by performing adjustment of the pressure in said raw material container at the temperature of said raw material container used with the formation process of said thin film.

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**DETAILED DESCRIPTION**

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[Detailed Description of the Invention]

[0001]

[Field of the Invention] this invention -- ALE (an atomic layer -- epitaxial) -- law and CVD (chemical vapor growth) -- law etc. evaporates a liquid or a solid material, and is supplied into a reaction chamber, and it is related with the approach of forming a thin film.

[0002]

[Description of the Prior Art] ALE (an atomic layer -- epitaxial) which supplies the former, for example, material gas, and purge gas on a substrate by turns -- he is trying to form a thin film on a substrate in law the liquid ingredient contained in the raw material container, or by supplying powdered or into the reaction chamber (reactor) in which the particulate-solid ingredient was evaporated, this was made into material gas, it let the path for material gas supply pass, and the substrate was installed in this material gas

[0003]

[Problem(s) to be Solved by the Invention] However, in the formation approach of the conventional thin film, by re-solidification of the material gas in the path for material gas supply, scattering of the raw material of the shape of powder out of a raw material container, etc., particle arises in the path for material gas supply, or a reaction chamber, and the problem that particle occurs on the substrate with which membrane formation is performed arises. This particle reduces remarkably engine performance of a thin film, such as lowering of withstand voltage, in the case where for example, an insulator thin film is formed.

[0004] Then, in view of the above-mentioned problem, this invention evaporates a liquid or a solid material, and supplies it into a reaction chamber, and it aims at reducing the particle in the path for material gas supply, or a reaction chamber in the formation approach of the thin film which forms a thin film.

[0005]

[Means for Solving the Problem] In order to attain the above-mentioned object, in invention according to claim 1 to 10 By letting the path for material gas supply pass, and supplying the material gas which evaporated the liquid or the solid material into the reaction chamber in which the substrate was installed By supplying inert gas to the interior of the path for material gas supply, and a reaction chamber in the shape of a pulse in front of the formation process of a thin film, in the approach of forming a thin film on a substrate, so that pressure fluctuation may be generated It is characterized by performing the clarification process which defecates the inside of the path for material gas supply, and a reaction chamber.

[0006] According to this invention, the particle which exists in the path for material gas supply and a reaction chamber can be blown away by generating pressure fluctuation before the formation process of a thin film, i.e., membrane formation initiation. Therefore, the particle in the path for material gas supply and a reaction chamber can be reduced.

[0007] Here, when two or more material gas supply systems are prepared, suppose that supply of inert gas was simultaneously performed in each material gas supply system. Then, the particle of different material gas which exists in the path for material gas supply of each \*\* may be simultaneously introduced in a reaction chamber, they may react mutually, and may generate new particle.

[0008] In that respect, according to invention of claim 2, it is characterized by shifting timing mutually and performing supply of inert gas by each material gas supply systems. Therefore, the particle of each material gas shifts timing, is introduced in a reaction chamber, and can reduce remarkably the particle newly generated by the reaction.

[0009] Especially, like invention of claim 3, if timing is shifted mutually and it is made to perform supply of inert gas by the material gas supply systems of a high combination of these reactivity when there is a reactant high combination among two or more material gas supply systems mutually, the effect of the invention of claim 2 can be demonstrated more certainly.

[0010] Moreover, invention of claim 4 is characterized by dividing timing mutually and performing supply of inert gas by the reducibility gas supply system and the oxidizing gas supply system, at a clarification process, when a material gas supply system is equipped with the reducibility gas supply system which supplies the material gas which has reducibility, and the oxidizing gas supply system which supplies the material gas which has an oxidizing quality. The particle mutually generated by the new reaction of the particle of reactant high reducibility gas and the particle of oxidizing quality gas by that cause can be reduced remarkably.

[0011] Furthermore, according to invention of claim 5, when there are a reducibility gas supply system and two or more oxidizing gas supply systems, respectively, supply of the above-mentioned inert gas can be summarized by reducibility gas supply systems and oxidizing gas supply systems, respectively, and can be performed. Therefore, the effect of the invention of claim 4 is efficiently realizable.

[0012] Moreover, according to invention of claim 6, it is characterized by shifting timing mutually and performing supply of inert gas by each supply system into two or more oxidizing gas supply systems, in two or more reducibility gas supply systems. Thereby, the particle generated by the new reaction of the particle of different material gas can be remarkably reduced from the same reason as invention of claim 2.

[0013] Moreover, after installing the substrate by which clarification was carried out after a clarification process and into a reaction chamber in invention of claim 7 and supplying inert gas like a clarification process, the process which measures the number of particle which adhered on the substrate is performed, and when there is few measured particle than the number of criteria, it is characterized by performing the formation process of a thin film. According to it, it can grasp certainly before membrane formation initiation by measuring the number of particle which adhered the effectiveness of the particle reduction by the clarification process on the substrate by which clarification was carried out.

[0014] Here, the number of particle 1 micrometers [ per two ] or more can set up the number of criteria according to claim 7 with one or less piece the unit area of 1cm of a substrate (invention of claim 8). Moreover, in invention of claim 9, it is characterized by performing a clarification process above the service temperature of the path for material gas supply in the formation process of a thin film. Since the particle formed by material gas can be made to re-evaporate by it, particle in the path for material gas supply can be made easy to blow away by pressure fluctuation, and it is effective.

[0015] Moreover, since pressure fluctuation generated by supply of the inert gas in a clarification process can be performed with more than the working pressure variation in the formation process of a thin film, i.e., the pressure fluctuation value added in the path for material gas supply, and a reaction chamber at the time of membrane formation, according to invention of claim 10, the particle which exists in the path for material gas supply and a reaction chamber can be blown away more certainly.

[0016] Moreover, although pulse-like supply of claim 1 thru/or inert gas according to claim 10 can be performed by closing motion of the bulb prepared in the path for inert gas supply etc. When the time amount which the change of closing motion of the bulb takes, the effectiveness which blows away the particle by pressure fluctuation are taken into consideration, even if the pulse is too short and it is too long, it is not practical, and it is desirable practically that it is 10 or less minutes 0.1 seconds or more (invention of claim 11).

[0017] Moreover, in the thin film formation approach which evaporates a liquid or a solid material, supplies into a reaction chamber, and forms a thin film, powdered or a particulate-solid raw material is made to evaporate, and there is a case supplied into a reaction chamber where it is contained in a

raw material container, by making this gas into material gas. In such a case, as mentioned above, there is a problem of particle generating by scattering of the raw material of the shape of powder out of a raw material container etc. Invention according to claim 12 to 16 relates to the thin film formation approach in such a case.

[0018] That is, in invention of claim 12 - claim 16, it is characterized by the thing which was contained in the raw material container and which supply inert gas in the shape of a pulse into a raw material container in front of the formation process of a thin film so that pressure fluctuation may be generated in powdered or the approach of forming a thin film on a substrate by supplying the material gas which evaporated the particulate-solid raw material into the reaction chamber in which the substrate was installed.

[0019] According to this invention, since the diameter of a granule or the raw material which has been easy being rolled lightly in a raw material container can be blown away and removed out of a raw material container by pressure fluctuation before membrane formation initiation, the particle in the path for material gas supply and a reaction chamber can be reduced as a result.

[0020] Here, it is desirable like invention of claim 13 to carry out pressure fluctuation generated by supply of inert gas to more than the working pressure variation in the formation process of a thin film. Thereby, since it is the same as that of invention of claim 10, and the diameter of a granule or the raw material which has been easy being rolled lightly in a raw material container can be more certainly blown away out of a raw material container in the formation approach of claim 12 and it can remove, the effectiveness of claim 12 can be demonstrated certainly.

[0021] Moreover, also in the formation approach of claim 12 and claim 13, since it is the same as that of invention of claim 11, it is desirable to perform supply of pulse-like inert gas so that the pulse may become 10 or less minutes 0.1 seconds or more (invention of claim 14).

[0022] Furthermore, in invention of claim 15, it is characterized by adjusting to less than  $20 \text{ kPa}$  of the pressure which is after the process which supplies inert gas in the shape of a pulse into a raw material container, and uses the pressure in a raw material container with the formation process of a thin film before the formation process of a thin film. According to it, the pressure in the raw material container in front of membrane formation initiation can be set to less than  $20 \text{ kPa}$  of the pressure used at the time of membrane formation.

[0023] If the pressure in the raw material container in front of membrane formation initiation was larger than  $20 \text{ kPa}$  of the pressure used at the time of membrane formation, when a raw material container is opened at the time of membrane formation and particle remains in the raw material container, possibility that this particle will go away from a raw material container to the path for material gas supply or a reaction chamber by the big pressure differential at the time of this disconnection is large. In that respect, in this invention, such a problem is avoidable as much as possible.

[0024] Here, as for adjustment of the pressure in a raw material container, it is desirable to carry out at the temperature of the raw material container used with the formation process of a thin film (invention of claim 16), and the effect of the invention of claim 15 can be demonstrated certainly. In addition, with the inert gas as used in the field of each above-mentioned invention, reactant low gas, i.e., the gas which does not participate in a reaction, is included to the material gas used for thin film formation besides rare gas or nitrogen gas.

[0025]

[Embodiment of the Invention] (The 1st operation gestalt) a \*\*\*\* 1 operation gestalt -- the formation approach of the thin film of this invention -- ALE (an atomic layer -- epitaxial) -- it explains as what was materialized to law. The outline block diagram of the ALE equipment applied to the 1st operation gestalt of this invention at drawing 1 is shown.

[0026] This ALE equipment supplies by turns the aluminum chloride ( $\text{AlCl}_3$ ), the titanium chloride ( $\text{TiCl}_4$ ), and water ( $\text{H}_2\text{O}$ ) which are material gas in a reactor (reaction chamber) 10 by the change of each bulb, and forms in a substrate 20 the thin film with which the laminating of an aluminum oxide (aluminum  $2\text{O}_3$ ) and the titanium oxide ( $\text{TiO}_2$ ) was carried out by turns.

[0027] In the ALE equipment shown in drawing 1, it has the aluminum chloride gas supply system 30, the titanium chloride gas supply system 40, and three water supply systems 50 for the material gas supply system for supplying material gas into the reactor 10 of the downstream. Each material

gas supply systems 30-50 have two paths of the paths 31, 41, and 51 for material gas supply for supplying material gas by making nitrogen (N<sub>2</sub>) gas into carrier gas from the upstream, respectively, and the paths 32, 42, and 52 for a purge which supply only nitrogen gas in order to purge the inside of a reactor 10.

[0028] Moreover, in each material gas supply systems 30-50, the raw material containers 33, 43, and 53 which contain the liquid (the titanium chloride, water) or solid material (aluminum chloride) used as the source of each material gas are intervened and formed in the section in the middle of the paths 31-51 for material gas supply. Moreover, the bypass paths 34, 44, and 54 which bypass the line which passes along the raw material containers 33-53 are established in each paths 31-51 for material gas supply.

[0029] Here, make the path between the upstream tee of the bypass paths 34-54, and the raw material containers 33-53 into the raw material container upstream paths 31a, 41a, and 51a among each paths 31-51 for material gas supply, and let the paths between the raw material containers 33-53 and the downstream unification section of the bypass paths 34-54 be the raw material container downstream paths 31b, 41b, and 51b. And the bulb which can open and close each path which is described below is prepared in each [ these ] material gas supply systems 30-50.

[0030] Namely, inclusion setting out of the 1st bulb A1, T1, and H1 is carried out at the section in the middle of each bypass paths 34-54. Inclusion setting out of the 2nd bulb A2, T2, and H2 is carried out at the section in the middle of each raw material container upstream paths 31a-51a. Inclusion setting out of 3rd bulb A3, T3, and H3 is carried out at the section in the middle of the raw material container downstream paths 31b-51b. In the middle of the paths 32-52 for a purge, inclusion setting out of 4th bulb A4, T four, and H4 is carried out at the section, and inclusion setting out of 5th bulb A5, and T5 and H5 is carried out between the downstream unification sections of the bypass paths 34-54 and the reactors 10 in each paths 31-51 for material gas supply.

[0031] The basic actuation in the film formation process of this ALE equipment using each [ these ] bulb is as follows. In this example, one layer of a multiple-times deed and an aluminum oxide is formed for 1 cycle (aluminum-oxide formation cycle) of an aluminum chloride gas supply -> nitrogen purge -> water supply -> nitrogen purge to the substrate 20 which was installed in the reactor 10 and heated by request temperature, exhausting a reactor 10 with a vacuum pump etc.

[0032] Next, one layer of a multiple-times deed and titanium oxide is formed for 1 cycle (titanium oxide formation cycle) of a titanium chloride gas supply -> nitrogen purge -> water supply -> nitrogen purge. An aluminum oxide and titanium oxide form the thin film (ATO film) by which crosswise lamination was carried out by repeating the stratification of these aluminum oxides and titanium oxide by turns.

[0033] In supplying material gas (an aluminum chloride, a titanium chloride, water), here In each material gas supply systems 30-50 the 1st bulb A1, T1, and H1 of a bypass path and 4th bulb A4 of the path for a purge, T four, and H4 A closed state, The 2nd remaining bulbs A2, T2, and H2, 3rd bulb A3, T3, H3 and 5th bulb A5, and T5 and H5 are made into an open condition.

[0034] Then, since the raw material in the raw material container 33-53 held at predetermined temperature has evaporated respectively (evaporation or sublimation), the material gas in these raw material container 33-53 passes along the paths 31-51 for material gas supply with nitrogen gas (carrier gas), and is supplied in a reactor 10.

[0035] On the other hand, in performing a nitrogen purge, only 4th bulb A4 of the path for a purge, T four, and H4 are made into an open condition, and it makes the 1st remaining the 3rd and 5th bulbs A1 - A3, A5, T1 - T3, T5, H1-H3, and H5 into a closed state. Then, only nitrogen gas passes along the paths 32-52 for a purge, and is supplied in a reactor 10. At this time, the 2nd and 3rd bulb A2 and A3 are good also as close.

[0036] Thus, although the formation process of a thin film is performed, in performing such a film formation process, in each paths 31-51 for material gas supply, or a reactor 10, the above-mentioned particle may remain by thin film formation to the last substrate etc. In the formation approach of the thin film of this operation gestalt, it is the object which removes this particle and a clarification process is performed before the formation process of a thin film (namely, before membrane formation initiation).

[0037] Fundamentally, this clarification process supplies inert gas (nitrogen gas) to the interior of the

paths 31-51 for material gas supply, and a reactor 10 in the shape of a pulse so that pressure fluctuation may be generated. The temperature of each raw material containers 33-53 and the temperature of a substrate 20 are held to a room temperature, and, specifically, each paths 31-51 and the temperature (piping temperature) of 32-52 are held to the laying temperature at the time of a film formation process (membrane formation).

[0038] Then, the 1st bulb A1, T1, and H1 of closing and a bypass path is first opened for the 2nd and 3rd bulbs A2 made open, A3, T2, T3, and H2 and H3 at the time of thin film formation. As for the inside of this clarification process, these bulbs A1 - A3, T1 - T3, and H1-H3 hold in the state of [ this ] always. Moreover, exhaust air of a reactor 10 is also always performed.

[0039] By this, only the nitrogen gas which is inert gas can be passed in each feeding systems 30-50 of this ALE equipment in the paths 31-51 for feeding, and reactor 10 grade. Moreover, 4th bulb A4 of the path for a purge, T four, H4 and 5th bulb A5 of the path for material gas supply, and T5 and H5 are closed first.

[0040] Next, it passes 3 slms of nitrogen gas at a time for 4th bulb A4 of each path for a purge, T four, and H4 to the paths 32-52 for a purge of an aperture and each feeding system. The flow of the nitrogen gas at this time is shown in the broken-line arrow head in drawing 1 , and does not flow in the paths 31-51 for material gas supply.

[0041] In addition, a nitrogen quantity of gas flow can supply the same flow rate now to each paths 31-51 for material gas supply, and the paths 32-52 for a purge by fixing with this value and changing 5th bulb A5 of the path for material gas supply, and T5 and H5. [ 4th bulb A4 of the path for a purge, T four, H4, and ]

[0042] Then, in order to perform cleaning of each paths 31-51 for material gas supply, and reactor 10 grade, pulse-like supply of nitrogen gas is performed. With this operation gestalt, since two or more material gas supply systems 30-50 which supply the material gas of a mutually different class are formed, timing is shifted mutually and it is made to perform supply of nitrogen gas by each 30 to material gas supply system 50 comrades. In this example, it is made to perform pulse-like supply of nitrogen gas in order of the aluminum chloride gas supply system 30, the titanium chloride gas supply system 40, and the water supply system 50.

[0043] First, in the aluminum chloride gas supply system 30, closing and 5th bulb A5 are opened for 4th bulb A4 for 0.5 seconds. The inside of the path 31 for material gas supply of the 5th bulb A5 downstream just before opening 5th bulb A5 is in the reduced pressure condition with the exhaust air in a reactor 10. Therefore, if 5th bulb A5 is opened for 0.5 seconds, as shown in the continuous-line arrow head in drawing 1 , nitrogen gas will flow the inside of the path 31 for material gas supply in the shape of a pulse.

[0044] Therefore, pressure fluctuation occurs inside the path 31 for material gas supply, and a reactor 10. Since the particle which remains in the path 31 for material gas supply and a reactor 10 can be blown away by this pressure fluctuation, the particle in the path 31 for material gas supply and a reactor 10 can be reduced.

[0045] Although the larger one of the pressure in the path 31 (piping) for material gas supply at this time is desirable, the positive crankcase ventilation valve (not shown) installed in the downstream of 5th bulb A5 adjusts it, for example, and it is made to become large from 20kPa. The flow rate of the line size which constitutes a path besides the above-mentioned positive crankcase ventilation valve, and inert gas etc. can adjust this pressure fluctuation value.

[0046] In this way, in the aluminum chloride gas supply system 30, after open Lycium chinense performs [ 4th bulb A4 ] pulse-like supply of nitrogen gas for closing and 5th bulb A5 for 0.5 seconds for 0.5 seconds, while closing 5th bulb A5, 4th bulb A4 is opened.

[0047] Then, in the titanium chloride gas supply system 40, pulse-like supply of nitrogen gas is performed for 0.5 seconds like the above. That is, if the 5th bulb T5 in the titanium chloride gas supply system 40 is opened for 0.5 seconds, as shown in the continuous-line arrow head in drawing 1 , nitrogen gas will flow the inside of the path 41 for material gas supply in the shape of a pulse. And after 0.5 seconds, while closing the 5th bulb T5, 4th bulb T four is opened.

[0048] Furthermore it continues and pulse-like supply of nitrogen gas is performed for 0.5 seconds like the above in the water supply system 50. That is, if the 5th bulb H5 is opened for 0.5 seconds, as shown in the continuous-line arrow head in drawing 1 , nitrogen gas will flow the inside of the path

51 for material gas supply in the shape of a pulse. And after 0.5 seconds, while closing the 5th bulb H5, a bulb four H4ths is opened.

[0049] Drawing 2 shows the timing of the inert gas (nitrogen gas) supply by the above-mentioned valve action. By not making 5th bulb A5 of the material gas supply systems 30-50, and T5 and H5 into an open condition at coincidence, respectively, but making 5th bulb A5, and T5 and H5 into an open condition one by one, timing is shifted every material gas supply system 30-50, and the pulse is supplied for nitrogen gas so that drawing 2 may show.

[0050] Supposing it performs supply of nitrogen gas simultaneously in each material gas supply systems 30-50, the particle of different material gas which exists in the paths 31-51 for material gas supply of each \*\*, or remaining material gas may be simultaneously introduced in a reactor 10, may react mutually, and may generate new particle. For example, the aluminum chloride which re-solidified and remains in piping may be supplied in a reactor 10 to timing simultaneous with the water which is easy to react, may react by the gaseous phase, and may form particle.

[0051] However, in order according to this operation gestalt to shift timing mutually and to perform supply of inert gas by each 30 to material gas supply system 50 comrades, the particle of each material gas blown away by pressure fluctuation shifts timing, and is introduced in a reactor 10.

[0052] Therefore, the particle (new generation particle) newly generated by the reaction can be reduced remarkably. And the cleaning effectiveness of each path or reactor 10 grade is acquired by repeating the pulse supply cycle of the nitrogen gas to these material gas supply systems 30-50 3000 times, for example. The above is a clarification process.

[0053] Although a substrate 20 may be set after this clarification process and a film formation process may be performed, a particle measurement process which is described below before a film formation process is further performed as a desirable gestalt of this formation approach. First, the substrate (clarification substrate) 20 by which clarification was carried out is installed in the substrate installation location after a clarification process and in a reactor 10, and the pulse supply cycle of nitrogen gas is performed 1000 times like the above-mentioned clarification process, for example.

[0054] Next, the number of particle adhering to the clarification substrate 20 is measured using a well-known particle measurement counter, it asks for the number of adhesion particle per unit area of this substrate 20, and when there is few called-for particle than the number of criteria, it moves to a film formation process. Here, if the practicability ability of a measuring instrument etc. is taken into consideration, as this number of criteria, the number of particle 1 micrometers [ per substrate 20 unit area ] or more can set one piece /as 2 cm.

[0055] And after checking becoming below this number of criteria, a film formation process (membrane formation) is started and the above-mentioned ATO film (2O3/TiO2 of aluminum cascade screen) is formed in this example. This ATO film is used as an insulating layer of for example, EL (electroluminescence) component. In addition, in a particle measurement process, if the measured number of particle becomes more than the number of criteria, a clarification process will be performed again.

[0056] Here, drawing 3 shows the particle consistency (piece/cm<sup>2</sup>) of 1 micrometers or more after membrane formation of the ATO film (this invention article) of this operation gestalt. In addition, the above-mentioned clarification process is not carried out to drawing 3, and the particle consistency after membrane formation of the ATO film (comparison article) which formed membranes in the condition that the measured number of particle of 1 micrometers or more is equivalent to two or more [ 10 //cm ] is also shown in it. From now on, with this operation gestalt, compared with a comparison article, a particle consistency is small a single figure and it will turn out that the particle after membrane formation can be reduced remarkably.

[0057] Moreover, drawing 4 shows the destructive field strength (V/cm) in the same ATO film as the above-mentioned this invention article and a comparison article. It turns out that lowering of the destructive field strength by particle reduction can be prevented according to this operation gestalt from now on. In addition, the flow rate indicated in the above-mentioned formation approach, the number of cycles, temperature, a pulse period, etc. are examples of this operation gestalt, and are not limited to this.

[0058] As mentioned above, according to this operation gestalt, it is characterized [ main ] by

reducing the above-mentioned new generation particle remarkably reducing the particle in the paths 31-51 for material gas supply, and a reactor 10 by generating pressure fluctuation before membrane formation initiation, and by shifting timing for every material gas supply system, and performing supply of nitrogen gas (inert gas).

[0059] Furthermore, according to the gestalt with this desirable operation gestalt, after a clarification process, since the particle measurement process described above before initiation of the formation process of a thin film is performed, it can grasp certainly before membrane formation initiation by measuring the number of particle which adhered the effectiveness of the particle reduction by the clarification process on the substrate by which clarification was carried out.

[0060] Moreover, it is desirable to perform temperature (piping temperature) of the paths 31-51 for material gas supply in a clarification process above the service temperature of the path for material gas supply in the formation process of a thin film. Since the particle formed by material gas can be made to re-evaporate by it, particle in the path 31-51 for material gas supply can be made easy to blow away by pressure fluctuation, and it is effective.

[0061] Incidentally, in the above-mentioned example, this piping temperature in a clarification process is made into the laying temperature at the time of membrane formation. In the path 31 for material gas supply of an aluminum chloride, as an example, 120-150 degrees C and the path 41 for material gas supply of a titanium chloride can make 50-60 degrees C and the path 51 for material gas supply of water temperature higher about 20 degrees C than the temperature which makes each raw material evaporate and generates material gas like 70-80 degrees C, for example.

[0062] Moreover, it is desirable to carry out pressure fluctuation generated by supply of the nitrogen gas (inert gas) in a clarification process to more than the working pressure variation in the formation process of a thin film, i.e., the pressure fluctuation value added in the paths 31-51 for material gas supply and a reactor 10 at the time of membrane formation. The particle which exists in the paths 31-51 for material gas supply and a reactor 10 can be blown away thereby more certainly.

[0063] (The 2nd operation gestalt) With the above-mentioned 1st operation gestalt, by the ALE method, each material gas of an aluminum chloride, a titanium chloride, and water was supplied in the reactor (reaction chamber) by turns, and the example which forms the crosswise lamination film of an aluminum oxide and titanium oxide was stated.

[0064] When there is a reactant high combination among two or more material gas supply systems mutually, by the material gas supply systems of a high combination of these reactivity, mutually, a \*\*\*\* 2 operation gestalt shifts supply of the inert gas in the above-mentioned clarification process, and is made to perform timing for it.

[0065] For example, corresponding to A, B, C, those with three kind, and each [ these ] material gas, three material gas supply systems have material gas, and although reactivity is high in Gas A and Gas B, the case where Gas A and Gas C have low reactivity is considered. In this case, if the particle of reactant high material gas A and B is simultaneously supplied to a reaction chamber, it will especially be easy to generate the above-mentioned new generation particle.

[0066] Then, the timing of the inert gas supply in the supply system of material gas A and material gas B is shifted at least. Thereby, the particle of each material gas A and B shifts timing, is introduced in a reaction chamber, and can reduce new generation particle remarkably.

[0067] As an example which has a reactant high combination mutually among such two or more material gas supply systems, there is an example which forms the aluminum-oxide film from the trimethylaluminum which is reducibility gas, and the water which is a oxidizing gas, for example. In this case, it is made to carry out by the trimethylaluminum gas supply system and water supply system which are material gas by shifting the timing of pulse-like supply of the above-mentioned inert gas.

[0068] Next, a material gas supply system explains the case where it has two or more reducibility gas supply systems which supply reducibility gas, and oxidizing gas supply systems which supply a oxidizing gas, respectively. In addition, there is the approach of forming the thin film used for the luminous layer of an EL element etc. (ZnS, Mn) as an example in this case, for example. This (ZnS, Mn) thin film supplies each material gas of diethylzinc, hydrogen-sulfide, and manganese chloride \*\* to a reaction chamber, makes it react suitably, and is formed.

[0069] Such a reducibility gas supply system and a oxidizing gas supply system are drawing

showing the timing of inert gas supply in case there are two or more pieces, respectively, and drawing 5 shows the case where there are a reducibility gas supply system and four oxidizing gas supply systems, respectively, by drawing 5. In drawing 5, four, G1-G4, are reducibility gas of the material gas, and four, G5-G8, are a oxidizing gas.

[0070] Here, although not illustrated, as a thin film deposition system of this operation gestalt, a material gas supply system can consider as the thing of a configuration of that eight pieces were prepared in the equipment shown in above-mentioned drawing 1 corresponding to eight different material gas of G1-G8. And like the above-mentioned 1st operation gestalt, by changing the bulb (equivalent to 4th bulb A4 of drawing 1 etc.) of the path for a purge, and the bulb (equivalent to 5th bulb A5 of drawing 1 etc.) of the path for material gas supply, inert gas can be supplied to the path for material gas supply in the shape of a pulse, and pressure fluctuation can be generated in each material gas supply system.

[0071] In the example shown in drawing 5, it is carrying out first by dividing mutually the timing of supply of inert gas (nitrogen gas, rare gas, etc.), and shifting it by the supply system (reducibility gas supply system) of reducibility gas G1-G4, and the supply system (oxidizing gas supply system) of oxidizing gases G5-G8. Thereby, the new generation particle by the particle of reactant high reducibility gas and the particle of oxidizing quality gas can be reduced remarkably mutually.

[0072] Moreover, according to drawing 5, first, about four reducibility gas supply systems (G1-G4) and four oxidizing gas supply systems (G5-G8), pulse-like supply of inert gas is summarized by reducibility gas supply systems and oxidizing gas supply systems, respectively, and is performed. Since the count which shifts the timing of inert gas supply by reducibility gas and the oxidizing gas can also be lessened by this, even if it can attain the increase in efficiency of a time process, it shifts and time amount, the time lag by the rate-of-flow error, etc. arise, both the particle of reducibility gas and oxidizing quality gas becomes that it is hard to be introduced to a reaction chamber simultaneously.

[0073] For example, although pulse-like supply of inert gas may be performed by turns like G1, G5, G2, G6, and ..... for every piece of a reducibility gas supply system and a oxidizing gas supply system, the count which shifts the timing of inert gas supply by reducibility gas and the oxidizing gas in this case increases. Then, since it becomes long in time, it will not be efficient, and possibility that both the particle of reducibility gas and oxidizing quality gas will be simultaneously introduced by the above-mentioned time lag etc. to a reaction chamber will also become large.

[0074] Furthermore, according to drawing 5, in order to make reduction of new generation particle into a more positive thing, in four summarized reducibility gas supply systems, inert gas supply is performed in the form which shifted timing mutually in every [ of further each ] supply system (G1-G4). This is the same also about four summarized oxidizing gas supply systems (G5-G8).

[0075] In addition, in drawing 5, the timing for every supply system of G1-G4 and every supply system of G5-G8 shifts, the timing between a oxidizing gas G4 and reducibility gas G5 shifts compared with a period K1, and the period K2 is long. The combination of this of a oxidizing gas and reducibility gas is clearer from the point of being easy to generate new generation particle than the combination of oxidizing quality gas or reducibility gas. Moreover, in drawing 5, although the oxidizing gas is previously performed for pulse-like supply of inert gas in timing, it is clear that reducibility gas may be performed first.

[0076] Moreover, in this operation gestalt, the effectiveness by performing the above-mentioned particle measurement process, performing piping temperature in a clarification process above the service temperature of the path for material gas supply in the formation process of a thin film, and carrying out pressure fluctuation generated by supply of the inert gas in a clarification process to more than the working pressure variation in the formation process of a thin film is acquired similarly.

[0077] (The 3rd operation gestalt) In the thin film formation approach which evaporates a liquid or a solid material, supplies into a reaction chamber, and forms a thin film, powdered or a particulate-solid raw material is made to evaporate, and there is a case supplied into a reaction chamber where it is contained in a raw material container, by making this gas into material gas. In such a case, as mentioned above, particle occurs by scattering of the raw material of the shape of powder out of a raw material container etc.

[0078] This operation gestalt aims at reducing the particle in a reaction chamber or the path for material gas supply by solving this problem. For example, the aluminum chloride in the above-mentioned 1st operation gestalt is that example, and the internal structure of the raw material container 33 of this aluminum chloride is typically shown in drawing 6. Hereafter, although a solid-state raw material is not limited to an aluminum chloride, suppose that it explains along with this drawing 6 and above-mentioned drawing 1.

[0079] In the raw material container 33, it is contained as particulate-solid raw material 33a, and this aluminum chloride serves as powdered or material gas evaporated by sublimation, and is supplied to the above-mentioned reactor 10. Here, in this operation gestalt, it is characterized by supplying nitrogen gas (inert gas) in the shape of a pulse into the raw material container 33, in front of the formation process of a thin film, so that pressure fluctuation may be generated.

[0080] In the aluminum chloride gas supply system 30 shown in above-mentioned drawing 1, the 2nd and 3rd bulbs A2 and A3 are made into an open condition, and, specifically, the 1st bulb A1 is made into a closed state. The raw material container 33 is made into the temperature (for example, room temperature) which the aluminum chloride which is a solid-state does not sublimate at this time. In this condition, 4th bulb A4 and 5th bulb A5 are changed, in the path 31 for material gas supply containing the raw material container 33, pulse-like supply of inert gas is performed and pressure fluctuation is generated.

[0081] Then, the diameter of a granule or aluminum chloride 33b which has been easy being rolled lightly which exists in the raw material container 33 can be blown away out of the raw material container 33. Blown-away aluminum chloride 33b is exhausted and removed through a reactor 10. Therefore, according to this operation gestalt, the amount of the particle supplied in the material gas supply path 31 or a reactor (reaction chamber) 10 in front of the inside of a formation process of a thin film (under membrane formation) can be reduced remarkably.

[0082] Especially the effectiveness at the time of in the case of the ALE method shown in the above-mentioned 1st operation gestalt, adopting this operation gestalt, in order to change the pressure in the raw material container 31 in order to supply nitrogen gas in the shape of a pulse, and to supply the diameter of a granule or the raw material (this example aluminum chloride) which has been easy being rolled lightly in the raw material container 31 to a reactor 10 also during membrane formation is large. Moreover, also in this operation gestalt, it is desirable to carry out pressure fluctuation generated by supply of inert gas like the above-mentioned 1st operation gestalt to more than the working pressure variation in the formation process of a thin film.

[0083] Moreover, it is desirable to adjust to the almost same value as the pressure which is after the process which supplies inert gas (nitrogen gas) in the shape of a pulse into the raw material container 31, and uses the pressure in the raw material container 31 with the formation process of a thin film before the formation process of a thin film with this operation gestalt. specifically making it less than \*\*20 kPas of the pressure used at the time of membrane formation -- it is desirable. For example, what is necessary is just to control the pressure fluctuation value by the last pulse to be set to less than \*\*20 kPas of the pressure used at the time of membrane formation, when performing the cycle which supplies inert gas in the shape of a pulse into the raw material container 31 two or more times.

[0084] By it, the pressure fluctuation at the time of membrane formation initiation can be reduced, and it can prevent that the diameter of a granule in the raw material container 31 or raw material 33b which has been easy being rolled lightly will be supplied to a reactor 10 by the pressure fluctuation at the time of membrane formation initiation. As for this pressure regulation process, it is desirable to perform temperature of the raw material container 31 in the condition of having considered as the temperature actually used at the time of membrane formation. By it, the factor to which the pressure fluctuation at the time of membrane formation initiation becomes large can be removed further.

[0085] (Other operation gestalten) In addition, what combined the above-mentioned 3rd operation gestalt and the above-mentioned 1st or 2nd operation gestalt may be used. It may be made to perform both the processes of the process which is got blocked, for example, supplies inert gas in the shape of a pulse into a raw material container before the formation process of a thin film, and a clarification process one by one (the execution sequence of both [ these ] processes is not asked).

[0086] Moreover, when the pulse-like supply of inert gas performed in each above-mentioned

operation gestalt takes into consideration the time amount which the change of closing motion of a bulb takes, the effectiveness which blows away the particle by pressure fluctuation, even if the pulse is too short and it is too long, it is not practical, and it is desirable practically that it is 10 or less minutes 0.1 seconds or more. In this way, this invention can supply inert gas in the shape of a pulse in the path for material gas supply, and a reaction chamber, and can perform effectively cleaning in a lifting, these paths, or a reaction chamber for pressure fluctuation intentionally. And this invention can evaporate a liquid or a solid material besides membrane formation of the luminous layer of the above-mentioned ALE method and an EL element etc., can supply it into a reaction chamber, and can be applied to the general approach of forming a thin film.

[Translation done.]

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**DESCRIPTION OF DRAWINGS**

[Brief Description of the Drawings]

[Drawing 1] It is the outline block diagram of the ALE equipment concerning the 1st operation gestalt of this invention.

[Drawing 2] It is drawing showing the pulse operation timing of the inert gas supply in the above-mentioned 1st operation gestalt.

[Drawing 3] It is drawing showing the particle consistency of the ATO film formed with the above-mentioned 1st operation gestalt.

[Drawing 4] It is drawing showing the destructive field strength of the ATO film formed with the above-mentioned 1st operation gestalt.

[Drawing 5] It is drawing showing the pulse operation timing of the inert gas supply in the 2nd operation gestalt of this invention.

[Drawing 6] It is drawing showing typically the internal configuration of the raw material container concerning the 3rd operation gestalt of this invention.

[Description of Notations]

10 -- A reactor (reaction chamber), 20 -- A substrate, 30, 40, 50 -- Material gas supply system, 31, 41, 51 -- The path for material gas supply, 31a, 41a, 51a -- Raw material container upstream path, 31b, 41b, 51b [ -- A bypass path, A1 - A5, T1-T5 H1-H5 / -- Bulb. ] -- A raw material container downstream path, 32, 42, 52 -- The path for a purge, 33, 43, 53 -- A raw material container, 34, 44, 54

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[Translation done.]

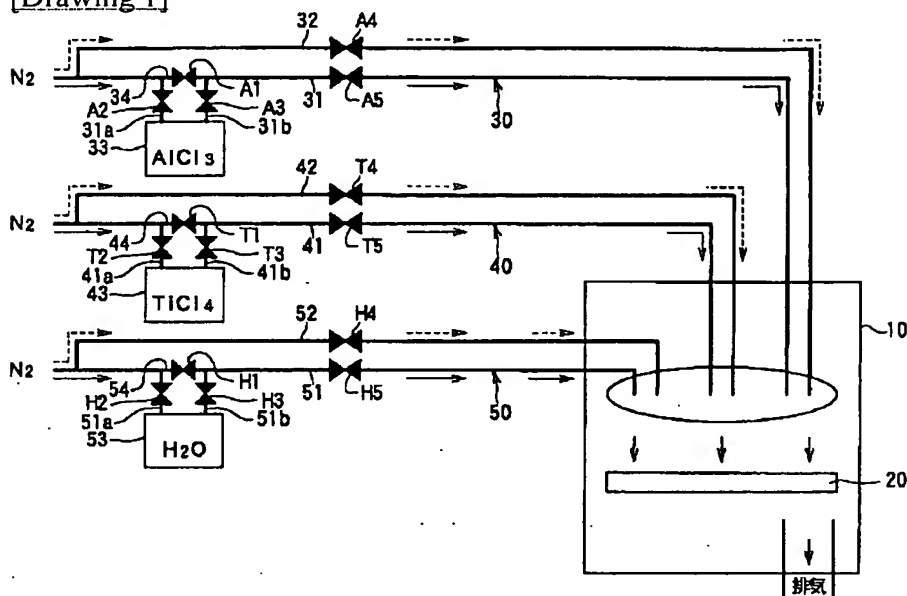
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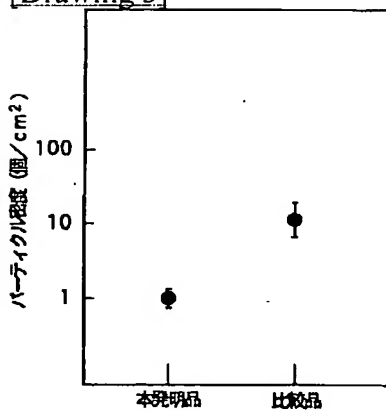
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## DRAWINGS

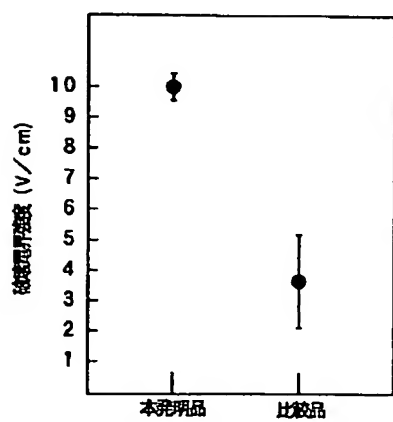
[Drawing 1]



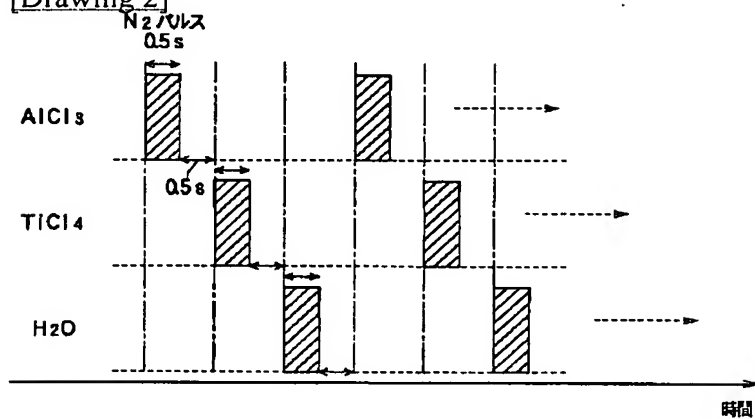
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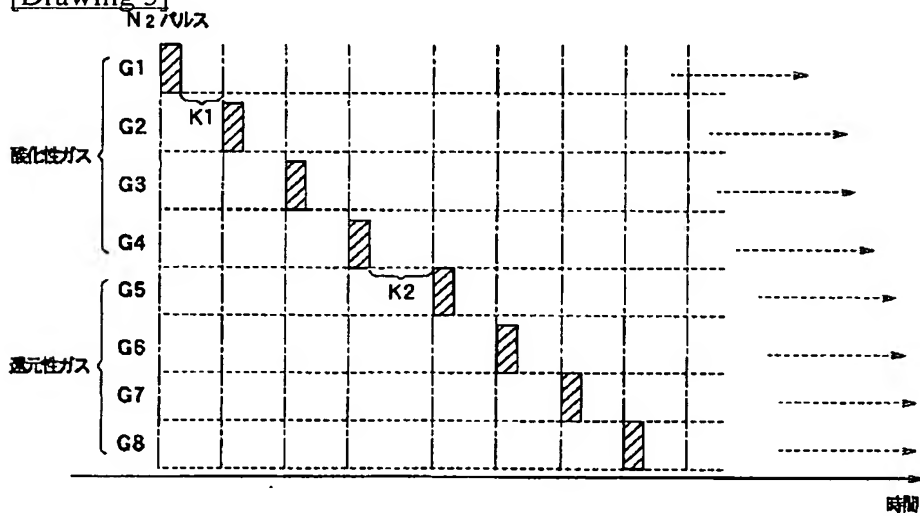
[Drawing 4]



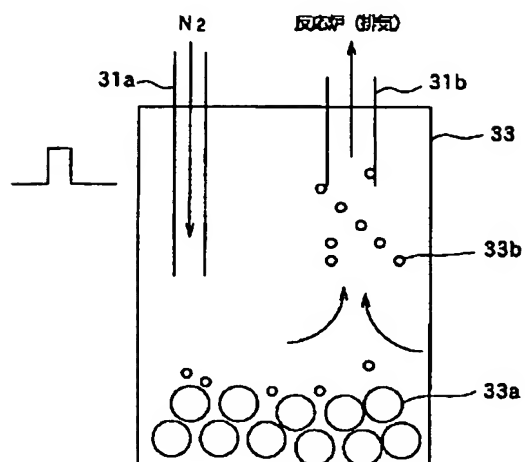
[Drawing 2]



[Drawing 5]



[Drawing 6]



[Translation done.]